SCIENCE FOR GLASS PRODUCTION

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CONDITIONS FOR PRODUCING AMBER AND BROWN GLASS

Yu. A. Guloyan[1]

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Dependences are identified that characterize redox reactions in the production of amber and brown glasses from batches using sodium sulfate with an excessive reducing agent or blast furnace slag. All reactions and resulting color shades are related to partial oxygen pressure. Boundary values for producing steady amber glasses are identified. The reducing potential of batches found by the oxydimetry method can be expressed via partial oxygen pressure, and it is recommended to determine this potential for tinted and clear glasses.

Imparting amber and brown colors to glass is commonly used in the production of glass containers. This tinting is achieved in the presence of iron oxides and sulfide sulfur and in a reducing atmosphere. Several researchers have investigated the nature of the amber chromophore and the conditions for its production [1, 2]. An integrated study of the amber chromophore established that its colorant complex consists of the central ion Fe^{3+} in the tetrahedral coordination surrounded by three ions of oxygen O^{2-} and one sulfide sulfur ion S^{2-}. It should be noted that raw materials used for producing tinted glass containers always contain iron oxides in quantities sufficient for imparting an amber tint.

It is known that sulfur in the course of amber glass melting may exist in different degrees of oxidation: S^{6+} (Na_2SO_4, SO_3), S^{4+} (SO_2), S^{2-} (Na_2S, FeS). The production of amber coloring is related to these transformations.

In our studies we used the known glass and batch compositions and added sodium sulfate with an excessive reducing agent or blast furnace slag containing sulfide sulfur. The content of iron oxides and sulfide sulfur was determined by chemical analysis. Furthermore, to estimate the final results, samples of melted glasses were prepared for spectrophotometric analysis.

The study mainly focused on studying the correlation between the redox conditions of the transformation of colorant compounds and the resulting tint. The experimental conditions and equipment were the same as described in [3, 4].

The main redox reactions during the decomposition of sodium sulfate in glass melting are as follows:

reduction of Na_2SO_4:

$$Na_2SO_4 + 2C = Na_2S + 2SO_2;$$

oxidation of Na_2S via an excess of Na_2SO_4:

$$Na_2S + 3Na_2SO_4 = 4Na_2O + 4SO_2.$$

In this case the required color shade is achieved with a certain ratio of Na_2SO_4 to the reducing agent and the potential (usually reducing) of the gaseous medium.

Blast furnace slag as a rule, contains sulfide sulfur compounds in an amount sufficient for the formation of the amber chromophore, but sometimes to get a required shade it is necessary to oxidize excessive sulfide sulfur by adding an oxidizer (usually Na_2SO_4) in accordance with the latter reaction.

Figure 1*a* shows the effect of partial oxygen pressure on the content of residual sulfide sulfur introduced via blast furnace slag. It can be seen that for partial oxygen pressure below 10^{-3} MPa the content of sulfide sulfur varies insignificantly.

It is interesting to analyze the variations in the content of sulfide sulfur and iron oxides when they are present simultaneously. This variation is important for getting an amber tint (Fig. 1*b*). In a reducing atmosphere the content of sulfide sulfur varies insignificantly, whereas the reduction of iron oxides proceeds more intensely. Thus, the preservation of sulfide sulfur in glass facilitates the reduction of iron oxides and increases the content of Fe^{2+} which does not participate in the formation of the amber chromophore [1].

Since reducing agents are introduced into amber glass batches and at the same time are contained in raw materials in the form of organic impurities, it is advisable to estimate the redox potential of the batch. This estimate performed by the oxydimetry method is based on the oxidation of organic compounds or sulfide sulfur in a sulfuric acid medium using potassium bichromate or permanganate. A subsequent titra-

[1] Research Institute of Glass, Gus'-Khrustalnyi, Vladimir Region, Russia.

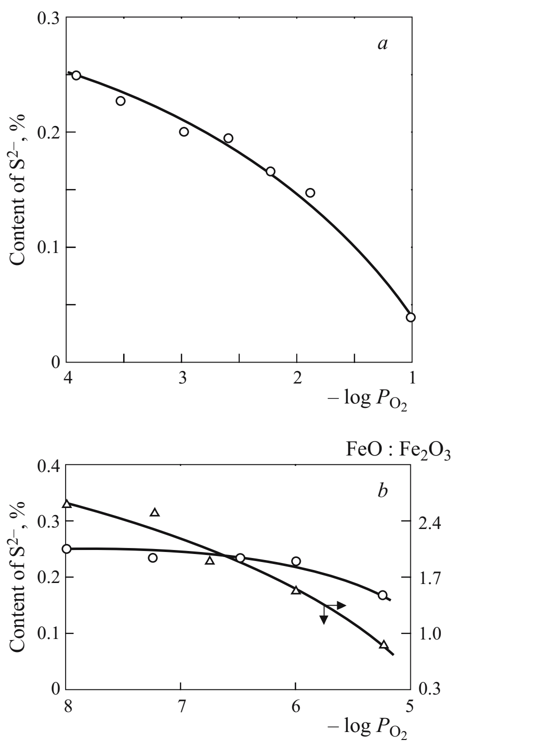

Fig. 1. Variations in sulfide sulfur content (a, b) and FeO : Fe_2O_3 ratio (b) versus partial oxygen pressure.

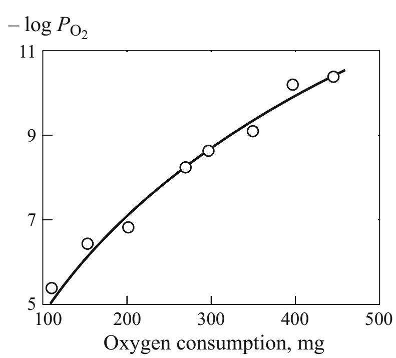

Fig. 2. Correlation between the reducing potential of the batch and partial pressure of oxygen.

tion using Moor's salt makes it possible to determine the amount of oxygen consumed on oxidizing the reducing agents in the batch. The higher the oxygen consumption, the higher is the reducing potential of the batch. This method was used to evaluate several experimental and industrial glass batches for container glasses with different contents of reducing agents. The maximum reducing potential was registered in the dark brown glass batch with excessive sulfide sulfur, which in industrial conditions has to be partly oxidized to obtain the required color and to avoid the formation of bubbles [2].

The oxydimetry method can be applied not only to tinted, but to clear glasses as well. When producing clear

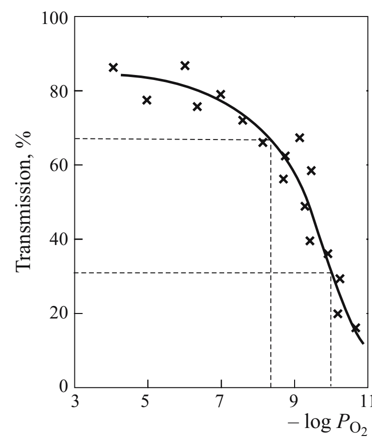

Fig. 3. Transmission of glass for wavelength 550 μm depending on the reducing potential of the medium.

glass products using standard materials, the latter may contain an increased amount of organic impurities facilitating the formation of small quantities of the amber chromophore which impair the light transmission of glass. Under certain conditions (excess of sulfates, a reducing regime) the formation of bubbles becomes possible. To prevent such consequence, it is necessary to minimize the content of organic impurities in initial materials, optimize the content of sulfate in the batch, and control the combustion regime.

To reveal the relationship between the reducing potential of the batch and the partial pressure of oxygen, comparative experiments were performed that involved heating batches with and without reducing agents under different reducing conditions of the gas atmosphere estimated by partial oxygen pressure. The comparison of results yielded a dependence shown in Fig. 2.

The obtained dependences and data on determining the reducing potential of experimental and industrial batches for container glasses make it possible to determined approximated bounds of partial oxygen pressure for producing amber and brown glass tints. The color of glass is characterized by spectral transmission at the wavelength of 550 μm. Depending on the reducing potential (partial oxygen pressure), the color of glasses varied from bluish-green to dark brown (Fig. 3). Despite a significant variance in experimental data, it is possible to identify the optimum range for amber coloring of glass. These conditions correspond to partial oxygen pressures ($-\log P_{O_2} = 8.5 - 10.0$), whereupon partial pressure that is near the lower bound produces dark glasses with decreased spectral transmission. In the interval of $-\log P_{O_2} = 7.0 - 8.3$ glasses have light yellow shades and above $-\log P_{O_2} = 7.0$ glasses are bluish-green. Below $-\log P_{O_2}$ glasses become very dark brown, unstable brown, and prone to the formation of numerous bubbles containing SO_2.

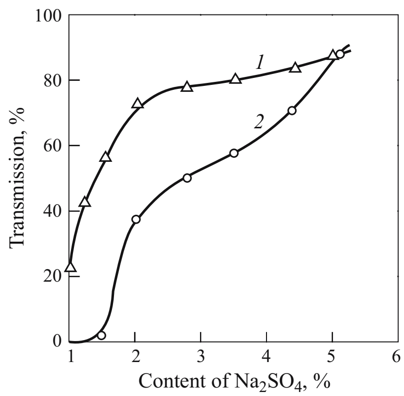

Fig. 4. Variation of selective transmission of glass for wavelength 550 μm (*1*) and 400 μm (*2*) depending on the amount of oxidizer.

It has been already mentioned that using blast furnace slag containing substantial quantities of sulfide sulfur, its excess has it be oxidized in order to control the color and to avoid bubbles. Usually sodium sulfate is used for oxidation. Figure 4 shows the effect of the amount of oxidizer on selective transmission of bottle glass melted with a constant content of blast furnace slag. The quantity of oxidizer corresponding to the initial points of the curves is accepted as unity. The glass has low spectral transmission at the wavelength of 550 μm, zero transmission at 400 μm, and a dark brown tint. As the content of oxidizer increases, the transmission first sharply and then smoothly increases with a corresponding modification of the tint. This indicates the destruction of the amber chromophore, as sulfur ligands become replaced by oxygen ones.

The present study has established the regularities characterizing the redox reactions in the production of amber and brown tint in glass. The obtained data make refine and enlarge the available database on amber tinting of glass.

Considering the importance of estimating the reducing potential of the batch, its determination in clear and tinted glasses can be recommended as a factor stabilizing the quality and service parameters of glass products.

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